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Influence of Ho^{3+} ions for quantitation of iron (Fe) in 0.1 M HCl solution using microwave plasma-atomic emission spectrometry (MP-AES)

Wpływ jonów Ho^{3+} na jakościowe oznaczanie żelaza w roztworze 0.1 M HCl metodą atomowej spektroskopii emisyjnej z plazmą mikrofalową (MP-AES)

Abstract
During research work in the Non-Ferrous Metals Department on AGH University of Science and Technology concerning new corrosion inhibitors for iron alloys in magnetic fields, Ho^{3+} ions were proposed as one of the new inhibitors. One of the methods for determining the rate of the corrosion process is determining the concentration of Fe ions in a solution. Due to the required high precision of determining the concentration of Fe ions in a solution contains Ho^{3+} ions with a wide range of concentrations, the influence of the matrix effect and interferences of Ho^{3+} ions must be known. The present work investigates the impact of Ho ions within a range of 0 to 100 mg/L for the quantitation of Fe ions in a 0.1 M HCl solution using the MP-AES method. The obtained results were analyzed using the single-factor ANOVA method. In a range of up to 40 mg/L, Ho^{3+} ions are not a significant factor to determining the Fe concentration by MP-AES.

Keywords: MP-AES, ANOVA, Fe, Ho3+

Streszczenie
W trakcie prac badawczych prowadzonych na Katedrze Fizykochemii i Metalurgii Metali Nieżelaznych na Akademii Górniczo-Hutniczej w Krakowie dotyczących nowych inhibitorów korozji stopów żelaza w polu magnetycznym, jako jeden z nowych inhibitorów zaproponowano jony Ho. Jedną z metod określenia postępów procesu korozji było oznaczenie stężenia jonów Fe w roztworze metodą atomowej spektroskopii emisyjnej w plazmie mikrofalowej (MP-AES). Z uwagi na wymaganą wysoką precyzję określenia niewielkiej zawartości jonów Fe w roztworach o różnej zawartości jonów Ho konieczne stało się zbadanie, czy obecność jonów Ho wpływa istotnie na ocenę ilościową jonów Fe metodą MP-AES. W niniejszej pracy zbadano wpływ stężenia jonów Ho w zakresie stężeń od 0 do 100 mg/l na oznaczenie zawartości Fe w 0,1 M kwasie solnym. Uzyskane

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wyniki poddano analizie statystycznej z wykorzystaniem metody ANOVA. W zakresie stężeń jonów Ho w analicie do 40 mg/L nie wykazano istotnego wpływu na oznaczenie żelaza na poziomie ufności 95%.

Słowa kluczowe: MP-AES, ANOVA, Fe, Ho3+

1. Introduction

Due to their good mechanical properties and relatively low cost, iron alloys in the form of steel are commonly used construction materials. They are a major component used in machines and ships construction, for example. One of the problems of exploiting this type of material is its quick failure due to its interaction with the environment (commonly called corrosion). One of the ways of reducing the rate of corrosion is to use inhibitors in the form of metal ions or organic compounds. During laboratory experiments of steel corrosion performed in solutions containing inhibitors, a quantitative determination of the iron ions in such a solution is necessary. Sometimes, the presence of additional elements or compounds in an analyzed solution can significantly affect the results of the analyte. The most commonly used methods of quantitatively determining the metal ions in a solution are inductively coupled plasma with mass spectrometry (ICP-MS), inductively coupled plasma with optical emission spectrometry (ICP-OES), microwave plasma with atomic emission spectrometry (MP-AES), and flame atomic absorption spectrometry (FASS). Both of the ICP methods are characterized by their high accuracy and precision, but they have relatively high operating costs [1]. MP-AES and FASS are much less expensive, but they provide problems with low matrix tolerance [2]. Moreover, MP-AES is a relatively new measuring technique (the first commercial MP-AES instrument was introduced in 2011 [3]); for this reason, the problems with matrix tolerance are not well--described. Furthermore, the MP-AES plasma temperature (up to 5000 K) [4] is lower than the plasma used in the ICP method (5000–10,000 K) [5]; therefore, it can reduce the numbers of fully ionized atoms, and it may not efficiently induce the thermal decomposition of the sample [1]. However, the temperature in MP is higher than the flame in the FASS technique (up to 3000 K) [6]; thus, the MP-AES method is more precise. In this paper, the matrix effect derived from Ho^{3+} ions on the quantitative determination of Fe has been studied. The spectral line of 371.993 nm (intensity of 16875.6) was primary selected by MP-AES as a main line for Fe determination. It also shows possible interferences with the Ho^{3+} ions at the spectral line of 372.132 nm (intensity 838.4). Moreover, the atomization and excitation of Fe may be influenced by the Ho^{3+} ions. It is possible to determine the iron from the another ion line (e.g., at 259.940 nm) with no spectral interferences [7]. However, the results obtained by Karlsson et al. [8] shows that a line at 259.940 nm may give an iron concentration of up to 40% (which is less than that determined with ICP-MS). The authors suggest that such behavior may result from the complexity of the matrix. During corrosion experiments with holmium ions used as corrosion inhibitors for iron, where the concertation of Ho ions may change within a wide range of concentrations

due to the matrix effect, and interferences may impact the quantitative iron determination. The matrix compensation technique or selective extractions require additional time, reagents, and workload, for sample preparation. Determining the iron within a range of holmium ion concentrations where the matrix affect is not present (where there is no significant difference) allows us to save a time and reduce the cost of the analysis.

2. Experiment

2.1. Iron calibration standard preparation

The calibration standard was prepared from 1000 mg·L^{-1} of an Fe solution in 2% HNO_3 (SPEX, CertiPrep, Metuchen, USA). The working standards were prepared at concentrations of 1 to 20 mg·L^{-1} by the serial dilution of standard solutions in 0.1 M HCl solutions. Hydrochloric acid at a 35–38% (m/V) purity for the analyses used for the whole experiment was produced by POCH. Deionized water (>18 mΩ) was obtained with HLP 5 (Hydrolab S.A., Straszyn, Poland). In all cases, the volume needed was taken using an Eppendorf Reference 2 pipet with a varied volume of up to 5 ml and transferred into a 50 mL volumetric flask (Class A, Glassco, India). In Table 1, the concentration of the calibration standards are shown. A suitable amount of Solution A was transferred to a 50 mL volumetric flask and filled up using 0.1 M HCl as a diluent. Solution A was obtained by a ten-fold dilution of the iron standard in 0.1 M HCl (Solution A contained 100 mg·L^{-1} Fe).

Table 1. Fe calibration standards

Standards	Fe [mg·L^{-1}]	Solution A [mL]
0	0.00	0.00
1	1.00	0.50
2	2.00	1.00
3	5.00	2.50
4	7.00	3.50
5	10.00	5.00
6	15.00	7.50
7	20.00	10.00

2.2. Holmium matrix preparation

To prepare the holmium matrix, 1.3564 g of holmium(III) chloride powder (99.9% and 200 mesh – Sigma Aldrich) was wetted by 1 mL deionized water in a glass beaker and dissolved in 1.50 mL $HClO_4$ (70% m/V) POCH. After 30 min, the obtained solution was brought to a 50 mL volumetric flask and made up to volume in deionized water. Next, the obtained 3.05 mL solution was transferred to a 50 mL volumetric flask and made up

with 0.1 M HCl. Finally, Solution B containing 1000 mg·L^{-1} was obtained. To prepare Solution C, Solution B was diluted ten-fold using 0.1 M HCl.

2.3. Sample preparation method

In order to receive the proper concentration of metals in the examined samples, Stock Solutions A, B, and C containing iron and holmium were mixed. According to the data from Table 2, the solution was transferred to a 50 mL volumetric flask and made up to volume using 0.1 M HCl. The concentration of Fe was set at 3.50 mg·L^{-1}. This value was selected for the following reason: the calibration curve for Fe is frequently prepared within a range of 1 to 20 mg·L^{-1}. Thus, the reference value in the experiments was selected at a level between 10–20% of the range.

Table 2. Analyzed sample preparation recipe

Sample	Fe [mg·L^{-1}]	Solution A [mL]	Ho [mg·L^{-1}]	Solution B [mL]	Solution C [mL]
0	3.50	1.75	0.00	0.00	0.00
1	3.50	1.75	1.00	0.00	0.50
2	3.50	1.75	2.00	0.00	1.00
5	3.50	1.75	5.00	0.00	2.50
7	3.50	1.75	7.00	0.00	3.50
10	3.50	1.75	10.00	0.00	5.00
15	3.50	1.75	15.00	0.00	7.50
20	3.50	1.75	20.00	1.00	0.00
40	3.50	1.75	40.00	2.00	0.00
60	3.50	1.75	60.00	3.00	0.00
80	3.50	1.75	80.00	4.00	0.00
100	3.50	1.75	100.00	5.00	0.00

2.4. Instrumentation

The microwave plasma atomic emission spectroscopy used in the experiment was facilitated by an Agilent MP-AES 4200 (Agilent Technologies, Santa Clara, CA, USA) equipped with the following:

- standard torch,
- OneNeb nebulizer,
- double-pass glass cyclonic spray chamber,
- Zefiro MP nitrogen generator (Cinel S.R.L., Vigonza, Italy).

In order to obtain stable reading measured samples, the MP-AES was run on deionized water for two hours before the proper measurement. The pump speed was set at 30 rpm for

30 s for the uptake sample. Also, the stabilization time (15 s) and pump speed (15 rpm) were set for torch stabilization. The spectral intensity registered was the average of five readings per sample. The read time was 3 s. For all samples, the measurements were repeated three times. The analytical wavelength (371.993 nm) and nebulizer flow (0.65 L·min^{-1}) were selected for the quantification of Fe, and the background correction was running in auto mode. In order to limit the impact of the device's time shift, a complete reslope was made after measuring eight samples. The order of the samples was chosen by lot without repetitions.

3. Results and statistical analysis

The parameters of the instrument work such as the linearity and slope of calibration curve were gathered in Table 3. For the used operation conditions, MP-AES showed excellent linearity with a coefficient of determination of $r^2 \geq 0.9999$ and standard deviation of the regression of $s_r < 800$. The signal stability in time (expressed as the relative error for signal intensity at the Fe 5.00 mg·L^{-1} calibration standard) does not exceed 4.00% during the whole measured time (a maximum value of 3.85% was obtained for comparing the values of Reslopes 1 and 5, and the time between Reslopes 1 and 5 was approx. 180 min.). The instrumental limit of detection (LOD) and limit of quantitation (LOQ) were determined based on the standard deviation for a blank signal peak. The LOD and LOQ values were determined using Equations (1) and (2):

$$LOD = \frac{SD_b \cdot 3}{m} \tag{1}$$

$$LOQ = \frac{SD_b \cdot 10}{m}, \tag{2}$$

where SD_b is the standard deviation for the blank signal and m is the slope of the standard calibration curve. The LOD and LOQ values for the determination of Fe with MP-AES were 5.58 μg·L^{-1} and 18.61 μg·L^{-1}, respectively. These values were similar to the values obtained by Li et al. [7]. In our case, line 371.993 nm gave approximately 55,000 counts for the 5.00 mg·L^{-1} Fe standards, while Karlsson et al. [8] obtained 33,800 counts used MP-AES 4100 using a nitric acid matrix.

Table 3. Impact of measurement time for linearity and slope of calibration curves for Fe analysis by MP-AES

Reslope	Calibration curve	r^2	s_r
1	$y = 11284 \cdot X - 87$	0.9999	776
2	$y = 10998 \cdot X - 126$	0.9999	677
3	$y = 10760 \cdot X + 162$	1.0000	445
4	$y = 10743 \cdot X + 261$	0.9999	692
5	$y = 10604 \cdot X + 147$	1.0000	531

The sample measurement results are collected in Table 4. The measured mean value of the reference sample without the Ho addition was equal to 3.45 mg·L^{-1}. The assumed value of the Fe was set to 3.50 mg·L^{-1}. This means that the relative error for the reference sample was equal to approx. 1.5%. Considering the random error made during the sample preparation and measurement process, the obtained value for the reference sample seems reasonable. Based on the calibration curve, the approximate measurement uncertainty can be estimated according to Equations (3)–(5) [9]. Assuming a statistical significance level of $\alpha = 0.05$ and a triple repeat of the measurements at each level of Ho^{3+} ion content, the determined content of iron in the samples should be on a level of $\mu_c = 3.50 \pm 0.12$ mg·L^{-1} (calculated for the data from the first calibration curve – see Table 3).

$$s_c = \frac{s_r}{m} \cdot \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_c - \bar{y})^2}{m^2 \cdot SS_{xx}}} \tag{3}$$

$$s_c = \frac{776}{11284} \cdot \sqrt{\frac{1}{3} + \frac{1}{8} + \frac{(38850 - 84541)^2}{(11284)^2 \cdot 354}} = 0.049 \tag{4}$$

$$\mu_{c_A} = c_A \pm t \cdot s_c = 3.45 \pm 2.47 \cdot 0.049 = 3.45 \pm 0.12 \tag{5}$$

where:

m – slope of calibration curve,
M – number of repeated sample,
N – number of calibration standards,
S_{xx} – variance of calibration standards,
$\bar{y}_c$ – signal mean value for measured sample,
$\bar{y}$ – signal mean value for calibration standards,
t – Student's t-distribution parameter for six degrees of freedom and $\alpha = 0.05$,
c_A – determined analyte concentration,
μ_{c_A} – mean value.

It is worth emphasizing that none of the results of iron concentration exceed 3.50 mg·L^{-1} in Table 4. This means that the applied method may have a tendency to underestimate the results. The results obtained from Equation (5) for the reference sample shows that the concentration of iron determined in the sample containing more than 40 mg·L^{-1} of Ho^{3+} exceeded the uncertainty range. Due to the results being obtained by using more than one calibration curve, computing the results using the ANOVA method is more precise and faster than determinations based on Equations (3) and (5). In order to check whether the influence of holmium ions on the determination the iron is significant, a single-factor ANOVA analysis was used.

Table 4. Contents of Fe determined by MP-AES of various Ho^{3+} ion content

Ho [mg·L^{-1}]	Fe [mg/l]				Error [%]
	repeat I	repeat II	repeat III	mean	
0	3.45	3.43	3.48	3.45	1.33
1	3.44	3.45	3.49	3.46	1.14
2	3.40	3.42	3.46	3.43	2.10
5	3.41	3.43	3.46	3.43	1.90
7	3.44	3.42	3.47	3.44	1.62
10	3.45	3.43	3.42	3.43	1.90
15	3.38	3.42	3.44	3.41	2.48
20	3.45	3.44	3.47	3.45	1.33
40	3.43	3.39	3.38	3.40	2.86
60	3.32	3.38	3.38	3.36	4.00
80	3.32	3.33	3.37	3.34	4.57
100	3.31	3.30	3.32	3.31	5.43

The analysis of variance (ANOVA) was performed at significant level of $\alpha = 0.05$ by using Matlab 2015a. The computations are summarized in the ANOVA table presented in Table 5. The obtained *F* value is equal to 11.2505, which is significantly higher than $F_{0.05,11,24} = 2.2163$. This means that there are at least two μ_i's that are significantly different from each other for $\alpha = 0.05$; thus, the Ho^{3+} ions in the sample affect the results. Due to the identify which of the μ_i's are different from one another. A Tuckey's HDS (Honest Significant Difference) multiple comparisons procedure were performed.

Table 5. Results of single-factor ANOVA procedure

Source of variation	*SS*	*df*	*MS*	*F*	Prob >*F*-	Test *F*
Treatments	0.078722	11	0.007157	11.2505	5.55E-07	2.216309
Error	0.015267	24	0.000636	–	–	–
Total	0.093989	35	–	–	–	–

The results of the calculation of the significant difference according to Tukey's HDS procedure (Eq. (6)) are gathered in Figure 1.

$$HDS_{0.05} = Q_{0.05,12,24} \cdot \sqrt{\frac{MSE}{I}} = 5.10 \cdot \sqrt{\frac{0.000636}{3}} = 0.074 \tag{6}$$

where:

Q – studentized range distributions parameter,

MSE – mean square error form ANOVA table (within groups error),

I – number of repeats for sample (number of observations).

The results show no significant differences in the determined iron concentration among the reference sample with the absence of Ho^{3+} ions (marked in red) and the samples with the presence of Ho^{3+} of up to 40 mg·L^{-1} (marked in grey). Only those samples containing 60, 80, and 100 mg·L^{-1} of Ho^{3+} are different (marked in blue).

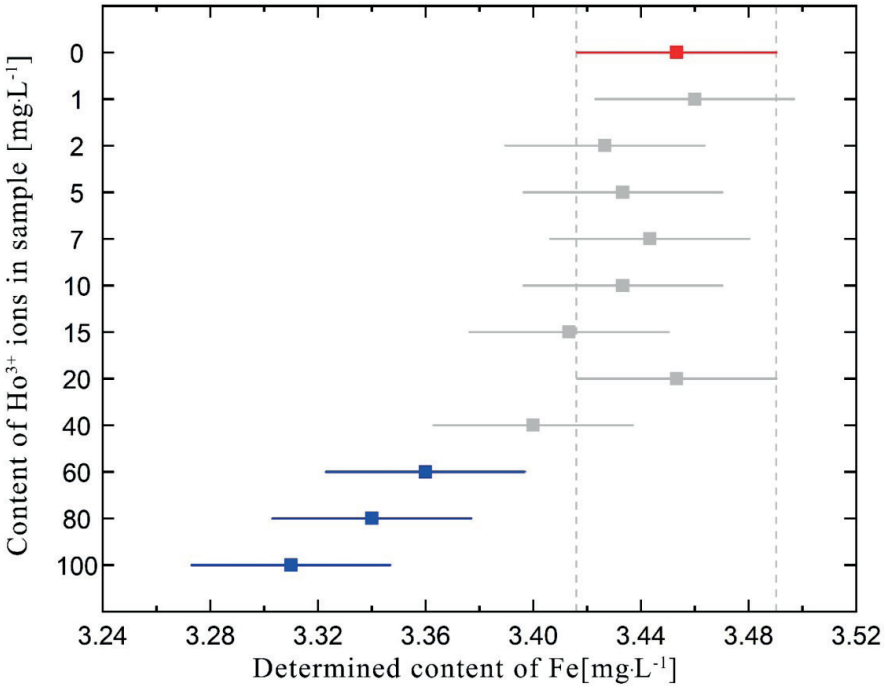

Fig. 1. Results of Tuckey's HSD multiple comparisons procedure: mean value of reference sample (red); mean value of significantly different samples from reference (blue); not significantly different (grey)

The tendency mentioned to underestimate the results is probably due to a combination of several factors. First, the sensitivity of the method decreases with measurement time – this is a normal phenomenon (see the decreasing slope of the calibration curve calculated in Table 3). This is related to the gradual very slow "clogging" of the nebulizer and contamination of the spray chamber. As a result, fewer atoms go directly to the torch. In order to prevent this affect, the device is recalibrated after analysis of a specific number of samples. In our case in the ANOVA table, decreasing the sensitivity during the measurements were revealed by increases in the error value. The addition of Ho^{3+} ions into the sample should theoretically increase the value of the analytical signal from the iron due to the close neighborhood of the spectral lines. In fact, the device works well

with analytical signal autocorrection and Ho^{3+} interference removed. The obtained lower value of Fe in the samples containing Ho^{3+} ions is probably due to the appearance of more atoms that must be excited in the torch.

4. Conclusions

A concentration of Ho^{3+} ions below 40 mg·L^{-1} did not significantly affect the determination of Fe concentrations in the tested samples with a confidence level of 95% for a spectral line of 371.993 nm by MP-AES. This means that the holmium ion concentration is about ten times greater that the determined iron concentration. In the discussion of the Ho^{3+} ion concentration range (0–40 mg·L^{-1}), the error between the set and the determined Fe concentration does not exceed 3%. Generally speaking, the increased holmium concentration in the matrix of the sample causes a decreased analytical signal from the iron. Summarizing, the iron determination method shown in this paper may have a tendency to underestimate the results.

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